Organic Chemistry

B.Sc I Year [Paper-II]

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Dr. Danveer Singh Yadav

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Preface

Organic chemistry is a specific discipline within the subject of chemistry. It is the scientific study of the structure, properties, composition, reactions, and preparation (by synthesis or by other means) of chemical compounds of carbon and hydrogen, which may contain any number of other elements, such as nitrogen, oxygen, halogens, and, more rarely, phosphorus or sulfur.

The electronic band structure (or simply band structure) of a solid describes ranges of energy that an electron is "forbidden" or "allowed" to have. It is due to the diffraction of the quantum mechanical electron waves in the periodic crystal lattice. The band structure of a material determines several characteristics, in particular its electronic and optical properties.

Organic chemicals get their diversity from the many different ways carbon can bond to other atoms. Carbon (C) appears in the second row of the periodic table and has four bonding electrons in its valence shell. Similar to other non-metals, carbon needs eight electrons to satisfy its valence shell.

Organic Chemistry is the study of the compounds of carbon, their reactions and their preparation. It is a fundamental course for the life sciences and chemical engineering. Traditionally, it is presented as a description of a large number of compounds classified by structure, and a few hundred typical reactions that will show how they can be prepared, and how they behave with respect to one another.

The reactions of inorganic chemistry usually take place in aqueous solution, where the water pulls apart the reagents into ions and allows them to move and interact freely. Occasionally reactions occur in fused reagents, between gases, or in the solid state where exchanges with the gaseous state can take place. The reactions are generally fast, and often go to completion. In organic

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chemistry, there are often other solvents than water, since most of the compounds are not soluble in water and do not form ions. Even where molecules are mobile, as in liquids and gases, reactions are often slow and incomplete. Even when a reaction is very exothermic, the reactants may not react.

In organic chemistry, an alkane, or paraffin (a historical name that also has other meanings), is an acyclic saturated hydrocarbon. In other words, an alkane consists of hydrogen and carbon atoms arranged in a tree structure in which all the carbon-carbon bonds are single.

An isomer of a molecule has the same number of atoms of each element, but has a different arrangement of the atoms. It has the same molecular formula as the other molecule, but with a different chemical structure. Isomers do not necessarily share similar properties, unless they also have the same functional groups. There are two main forms of isomerism : structural isomerism (or constitutional isomerism) and stereoisomerism (or spatial isomerism).

Alkanes are usually stable at room temperature toward reactants such as concentrated aqueous acids or bases, an even the most reactive metals. Fluorine, however, attacks virtually all organic compounds, including the alkanes, to give mixtures of products.

The book is presented and organized in a way to discourage students from rote learning. It covers all the topics in Organic Chemistry which are normally included in the syllabi of Indian universities for undergraduate courses.

—Dr. Danveer Singh Yadav

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1

Structure and Bonding

BAND STRUCTURE OF ELECTRONIC

The electronic band structure (or simply band structure) of a solid describes ranges of energy that an electron is "forbidden" or "allowed" to have. It is due to the diffraction of the quantum mechanical electron waves in the periodic crystal lattice. The band structure of a material determines several characteristics, in particular its electronic and optical properties.

Bands occur in materials

The electrons of a single free-standing atom occupy atomic orbitals, which form a discrete set of energy levels. If several atoms are brought together into a molecule, their atomic orbitals split, as in a coupled oscillation. This produces a number of molecular orbitals proportional to the number of atoms. When a large number of atoms (of order 1020 or more) are brought together to form a solid, the number of orbitals becomes exceedingly large, and the difference in energy between them becomes very small, so the levels may be considered to form continuous bands of energy rather than the discrete energy levels of the atoms in isolation. However, some intervals of energy contain no orbitals, no matter how many atoms are aggregated, forming band gaps.

Within an energy band, energy levels are so numerous as to be a near continuum. First, the separation between energy levels in a solid is comparable with the energy that electrons constantly exchange with phonons (atomic vibrations). Second, it is

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comparable with the energy uncertainty due to the Heisenberg uncertainty principle, for reasonably long intervals of time. As a result, the separation between energy levels is of no consequence.

Basic Concepts

Any solid has a large number of bands. In theory, it can be said to have infinitely many bands. However, all but a few lie at energies so high that any electron that reaches those energies escapes from the solid. These bands are usually disregarded. Bands have different widths, based upon the properties of the atomic orbitals from which they arise. Also, allowed bands may overlap, producing (for practical purposes) a single large band. Metals contain a band that is partly empty and partly filled regardless of temperature. Therefore they have very high conductivity. The lowermost, almost fully occupied band in an insulator or semiconductor is called the valence band by analogy with the valence electrons of individual atoms. The uppermost, almost unoccupied band is called the conduction band because only when electrons are excited to the conduction band can current flow in these materials.

The difference between insulators and semiconductors is only that the forbidden band gap between the valence band and conduction band is larger in an insulator, so that fewer electrons are found there and the electrical conductivity is lower. Because one of the main mechanisms for electrons to be excited to the conduction band is due to thermal energy, the conductivity of semiconductors is strongly dependent on the temperature of the material. This band gap is one of the most useful aspects of the band structure, as it strongly influences the electrical and optical properties of the material. Electrons can transfer from one band to the other by means of carrier generation and recombination processes. The band gap and defect states created in the band gap by doping can be used to create semiconductor devices such as solar cells, diodes, transistors, laser diodes, and others.

Symmetry

A more complete view of the band structure takes into account the periodic nature of a crystal lattice using the

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symmetry operations that form a space group. The Schrφdinger equation is solved for the crystal, which has Bloch waves as solutions:

$$\frac{1}{2}_{nk}(r) = e^{ik.r}u_{nk}(r),$$

where *k* is called the wavevector, and is related to the direction of motion of the electron in the crystal, and n is the band index, which simply numbers the energy bands. The wavevector k takes on values within the Brillouin zone (BZ) corresponding to the crystal lattice, and particular directions/points in the BZ are assigned conventional names like Γ, Δ, Λ, Σ, etc. These directions are shown for the face-centred cubic lattice geometry.

The available energies for the electron also depend upon k, for silicon in the more complex energy band diagram at the right. In this diagram the topmost energy of the valence band is labeled Ev and the bottom energy in the conduction band is labeled Ec.

The top of the valence band is not directly below the bottom of the conduction band (Ev is for an electron travelling in direction Γ, Ec in direction X), so silicon is called an indirect gap material. For an electron to be excited from the valence band to the conduction band, it needs something to give it energy Ec "Ev and a change in direction/ momentum. In other semiconductors (for example GaAs) both are at Γ, and these materials are called direct gap materials (no momentum change required). Direct gap materials benefit the operation of semiconductor laser diodes. Anderson's rule is used to align band diagrams between two different semiconductors in contact.

Band Structures in Different Types of Solids

Although electronic band structures are usually associated with crystalline materials, quasi-crystalline and amorphous

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solids may also exhibit band structures. However, the periodic nature and symmetrical properties of crystalline materials makes it much easier to examine the band structures of these materials theoretically. In addition, the well-defined symmetry axes of crystalline materials makes it possible to determine the dispersion relationship between the momentum (a 3-dimension vector quantity) and energy of a material. As a result, virtually all of the existing theoretical work on the electronic band structure of solids has focused on crystalline materials.

Density of States

While the density of energy states in a band could be very large for some materials, it may not be uniform. It approaches zero at the band boundaries, and is generally highest near the middle of a band. The density of states for the free electron model in three dimensions is given by,

$$D(\in) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \in^{1/2}$$

Filling of Bands

Although the number of states in all of the bands is effectively infinite, in an uncharged material the number of electrons is equal only to the number of protons in the atoms of the material. Therefore not all of the states are occupied by electrons ("filled") at any time. The likelihood of any particular state being filled at any temperature is given by the Fermi-Dirac statistics.

The probability is given by the following:

$$f(E) = \frac{1}{1 + e\dfrac{E - E_F}{k_B T}}$$

where:

- k_B is Boltzmann's constant,
- T is the temperature,
- E_F is the Fermi energy (or 'Fermi level').

The Fermi level naturally is the level at which the electrons and protons are balanced.

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At T = 0, the distribution is a simple step function:

$$f(E) = \begin{cases} 1 & \text{if } 0 < E \leq E_F \\ 0 & \text{if } E_F < E \end{cases}$$

At nonzero temperatures, the step "smooths out", so that an appreciable number of states below the Fermi level are empty, and some states above the Fermi level are filled.

BASIC BONDING CONCEPTS

The most basic concept in all of chemistry is the chemical bond. The chemical bond is essentially the sharing of electrons between two atoms, a sharing which holds or bonds the atoms together. In order to understand the chemical bond, atoms and electrons must first be understood.

Electron Orbitals

Atoms have three components: protons, neutrons, and electrons. Protons have a positive charge of +1, neutrons have 0 charge, and electrons have a negative charge of -1. The protons and neutrons occupy the centre of the atom as a piece of solid matter called the nucleus.

The electrons exist in "orbitals" surrounding the nucleus. In the olden times, it was believed that the electrons orbited the nucleus in the same way that planets orbit the sun.

This is not exactly true, but it explains the origin of the term orbital to describe the location of the electron. In reality, it is impossible to tell the precise trajectory of an electron in the way that the path of a planet can be followed. The best that can be achieved is to describe the probability of locating the electron in a region of space.

The distribution of this probability over space is called an orbital. Let us treat the simplest case, in which the nucleus is surrounded by just one electron (for example, the hydrogen atom).

In this case, the probability of finding an electron in its lowest energy, or most stable, state is distributed in a spherically symmetric way around the nucleus. The probability of finding the electron is highest at the nucleus and decreases as the distance from the nucleus increases.

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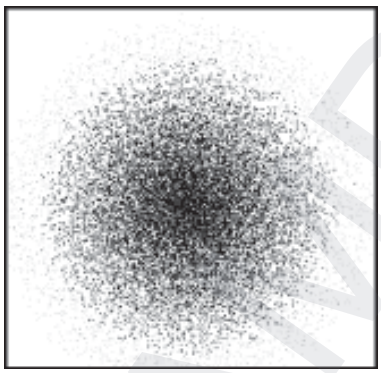


Figure: ***1s Orbital***



Figure: ***2p Orbital***

The density of dots in a region represents to the probability of locating the electron there. This lowest energy, spherically symmetric orbital is called the 1s orbital. As stated, in this orbital, the highest probability of finding the electron at a point in space occurs at the nucleus. Such a location may seem counterintuitive, since the electron is known to generally be located some distance from the nucleus, not directly at it. How can this apparent contradiction be explained?

Although the probability of finding the electron at a point is greatest at the nucleus, the volume of space occupied by the nucleus is extremely small compared to the rest of the atom.

The probability of finding the electron at a point decreases farther from the nucleus, but the volume in which it can be found becomes much, much larger. So the electron is more likely to be found some distance from the nucleus. It is the product

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